

Molecular studies of self assembled monolayers as corrosion inhibitors for copper

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Due to its high thermal and electrical conductivity copper has found many industrial applications, such as in heat exchangers and electrical contacts. However, copper suffers from oxidation and corrosion in contact with corrosive atmospheres, which can result in failure or decrease in efficiency of equipments or components. Indoor corrosion of copper can have detrimental effects on performance, and the most important corrosion stimulators for copper have been identified, e.g. humidity, oxygen and carboxylic acids.¹

To protect the surface from corrosion or oxidation various organic and inorganic coatings have been proposed. Self assembled monolayers (SAMs) of alkanethiols have been found to be promising candidates as corrosion inhibitors for copper, due to their ease of application, spontaneous adsorption and their nanometer thickness. The latter is very important in applications where thickness may be an important property, such as in microelectronics and micromechanics.² While SAMs based on alkanethiols have been thoroughly studied, SAMs based on the structurally related alkaneselenols have been studied to a much lesser extent.

In the present work the ability of SAMs (alkanethiols and alkaneselenols) with different chain length has been explored as corrosion inhibitors for copper in humid air with sub-ppm concentrations of formic acid, an atmosphere that mimics indoor corrosion conditions. To follow the formation of different corrosion products on SAM-covered copper, a near-surface sensitive technique, infrared reflection adsorption spectroscopy (IRAS), was used in-situ to monitor the nature of corrosion products, both qualitatively and quantitatively. To assess the quality of the SAMs initially deposited on copper, as well as to follow their structural change during exposure, a truly interface sensitive technique was used ex-situ, vibrational sum frequency spectroscopy (VSFS). The combination of VSFS and IRAS enabled us to correlate changes in molecular structure and conformation of the SAMs to the kinetics of corrosion product formation. The GILDES model,³ a multiregime computer model which involves the gas phase (G), the gas/liquid interface (I), the liquid phase (L), the deposition layer (D), the electrodic region near the surface (E), and the solid phase (S) was then used to explain different mechanisms involved in the initial stage of SAM covered copper corrosion under current exposure conditions.

For alkanethiol covered samples, a full suppression of copper (I) oxide formation and a delay in copper formate and copper hydroxide formation was observed when comparing with bare copper exposed to the same corrosive atmosphere. This was attributed to a selective hindrance of the corrosion stimulators oxygen gas, water and formic acid to penetrate through each SAM. The delay in copper formate and copper hydroxide formation increased with increasing SAM chain length. All SAMs investigated preserved their protective structure during exposures of up to a few days, and only small increases in structural disorder, as measured by the presence of gauche defects in the SAMs, was observed after longer exposure

period.⁴

For alkaneselenol-covered copper, on the other hand, the formation of copper (I) oxide was observed. This can be attributed to the local removal of alkaneselenol-based SAMs upon exposure to the corrosive atmosphere.

References:

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